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(54) Highly absorbent polymer

(57) A highly absorbent polymer comprises water-insoluble, hydrophilic, crosslinked polymer particles having carboxyl or carboxylate groups, characterised in that said water-insoluble, hydrophilic, crosslinked polymer particles have an absorbing capacity satisfying the following requirements (i) to (iii), said absorbing capacity being imparted by enhancing the crosslinking density of the surfaces of said water-insoluble, hydrophilic, crosslinked polymer particles:

- (i) the equilibrium swelling physiological saline absorption is 40 g/g (polymer) or more;
- (ii) the physiological saline absorption is 3 ml or more as determined by swelling 0.3 g of the polymer with physiological saline for 10 sec; and
- (iii) the time taken for 5ml of physiological saline to pass through a cylinder (internal diameter: 10mm) having a cross-sectional area of 0.785 cm<sup>2</sup> is 40 sec or less after 0.05 g of the polymer is packed together with physiological saline into the cylinder and swollen with the physiological saline, reaches an equilibrium swelling physiological saline absorption and settles in a swollen state.

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FIG.1

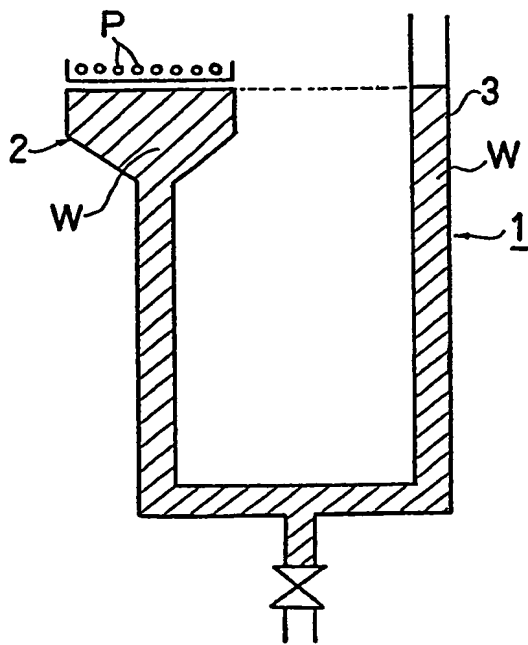
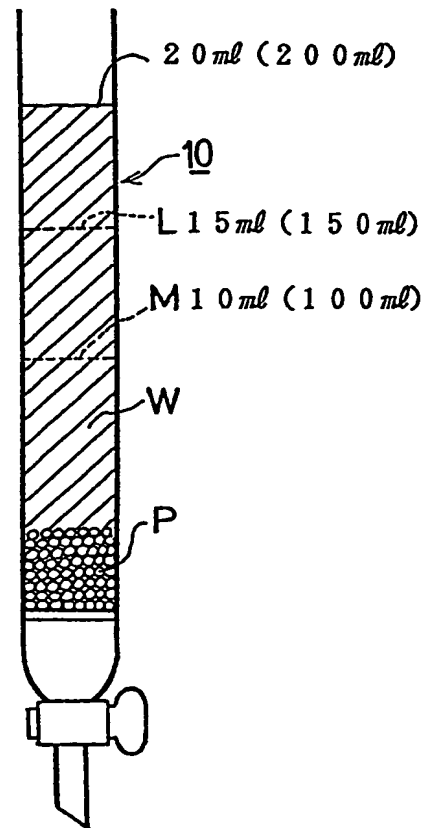


FIG.2



## HIGHLY ABSORBENT POLYMER

## BACKGROUND OF THE INVENTION

## [Field of the Invention]

The present invention relates to a highly absorbent polymer, more particularly, to a highly absorbent polymer which exhibits a high initial rate of absorption of a large amount of an aqueous liquid, such as a body fluid, is free from the lowering in the absorbing capacity after the initial absorption and can sufficiently exhibit the absorbing capacity of the absorbent polymer when used as an absorbent material such as a disposable diaper.

## [Description of the Prior Art]

Paper, pulps, sponges, etc., have hitherto been used as a water absorbing or water holding material in the field of sanitary materials (sanitary napkins, paper diapers, etc.) and agriculture and forestry. These materials, however, have a poor water absorbing capacity, and a considerable amount of the water absorbed by these materials are easily squeezed out when a pressure is applied.

For this reason, in recent years, absorbent polymers, such as a hydrolysate of starch/acrylonitrile graft polymer, a crosslinked product of polysodium

acrylate, a modified cellulose ether and a hydrolysate of a methyl acrylate/vinyl acetate copolymer, have been proposed as an absorbent material alternative to the above-described materials, and their modified products have also been proposed.

Conventional main methods for producing absorbent polymers comprise crosslinking a water-soluble polymer to a small extent to render the polymer water-insoluble, and the following crosslinking methods have been proposed in the art:

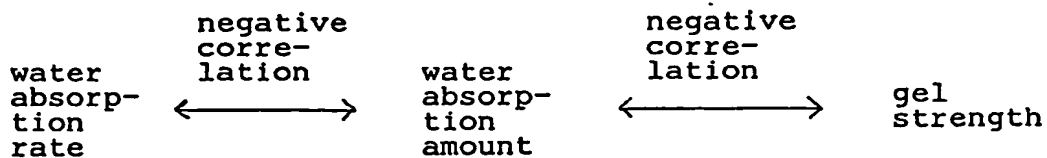
(1) self-crosslinking is conducted through the optimization of the production conditions, and

(2) a crosslinking agent is added during or after the polymerization to conduct crosslinking.

Although some absorbent polymers produced by the above-described methods have excellent properties, they cannot satisfy all the properties required of the absorbent polymer.

Specifically, examples of the performances required of the absorbent polymer include (1) water absorption, (2) water absorption rate and (3) gel strength. It is generally recognized that there exists the following relationship between these properties. The conventional absorbent polymers have been produced so as to form a structure capable of offering

a balance of the following relationships, so that the structure is such that individual properties are each slightly sacrificed.



Further, various proposals have been made on an improvement in the above-described property requirements for the absorbent polymer, and these are various documents disclosing these proposals. Specifically, Japanese Patent Laid-open Nos. 161413/1981 and 1205/1985, etc., disclose an invention directed to an improvement in the absorbing capacity (an improvement in the water absorption), Japanese Patent Publication Nos. 18690/1985 and 74241/1991, Japanese Patent Laid-open No. 9730/1986, etc., disclose an invention directed to an improvement in the capability of the absorbent polymer to rapidly absorb a liquid (an improvement in the water absorption rate), and Japanese Patent Laid-Open No. 185550/1985, etc. disclose an invention directed to an improvement in the particle strength after swelling (an improvement in the gel strength). Further, besides the above-described publications, Japanese Patent Laid-open Nos. 62463/1986 and 28639/1988 and Japanese Patent Publication Nos. 40623/1991 and

742141/1991, etc., disclose an invention directed to an improvement in the absorbent polymer.

However, all the conventional means for modifying an absorbent polymer are limited to an improvement in the absorbing capacity of the absorbent polymer in a period between the initial aqueous liquid absorption of the absorbent polymer in the contact of the absorbent polymer with the aqueous liquid and the equilibrium of swelling, and no consideration is given to an improvement in the function of the absorbent polymer in the practical use in sanitary articles such as disposable diapers and sanitary napkins, particularly an improvement in the absorbing capacity where, after the aqueous liquid absorption, the polymer absorbs again the aqueous liquid.

When use is made of sanitary articles provided with an absorbent polymer, the absorbent polymer exhibits the following function. The absorbent polymer usually absorbs an aqueous liquid to the full upon contact with the aqueous liquid, the aqueous liquid absorption is stopped with the polymer still having an absorbing capacity, and then the polymer again absorbs an aqueous liquid which has freshly come into contact with the absorbent polymer. In this mode of actual use, it is difficult for the absorbent polymers to

sufficiently exhibit their absorbing capacity, so that, in actual use, excellent function and effect in respect of the absorbing capacity cannot be attained even in diapers and sanitary napkins using an absorbent polymer having an excellent absorbing capacity (that is, an absorbent polymer which exhibits a high value in the measurement of the absorbing capacity by an instrument).

A main cause by which it becomes difficult for the absorbent polymer to satisfactorily exhibit its absorbing capacity includes the occurrence of an absorption blocking phenomenon (gel blocking) caused by an interaction between absorbent polymers swollen through the absorption of an aqueous liquid such as a body fluid. It is recognized that the gel blocking becomes significant in proportion to the initial absorption rate of the absorbent polymer.

Specifically, when the absorbent polymer is brought into contact with an aqueous liquid, such as a body fluid, to absorb the aqueous liquid, the higher the initial absorption rate, the shorter the time taken for the polymer to be swollen and softened in a limited narrow region for contact with the aqueous liquid and the larger the amount of the aqueous liquid in the limited narrow region. As a result, the absorbent

polymers come into mutual contact with each other due to swelling and softening, or they are mutually adhered due to rearrangement thereof, which causes the volume voids defined by swollen polymers to be reduced. This in turn causes the void portion as a passage for the body fluid to be blocked, so that a liquid layer is formed in this portion, that is, gel blocking occurs. Therefore, in the absorbent polymer which has once absorbed an aqueous liquid, the above-described gel blocking serves as a barrier, so that the absorbent polymer which has again come into contact with the aqueous liquid does not contribute to the absorption even when the absorption does not reach a saturated state.

In general, the main cause of the occurrence of gel blocking is considered to include (1) a reduction in voids between particles and (2) occurrence of tackiness on the outer walls of particles in a swollen state of the absorbent polymer. For the above-described reason, the liability of occurrence of gel blocking increases in proportion to the initial absorption rate of the absorbent polymer. Therefore, the use of an absorbent polymer having an improved initial absorption rate in absorbent articles does not always contribute to the effect of suppressing leakage in the



absorbent articles.

As is well known in the art, it is needless to say that, as compared with absorbent polymers having a high initial absorption rate, absorbent polymers having a low initial absorption rate have various problems.

Further, an increase in the amount of the absorbent polymer has been conducted for the purpose of improving the absorbing capacity of absorbent articles. In such a constitution, the distance between particles of the absorbent polymer becomes so small that the absorbent polymer is in a state susceptible to gel blocking.

#### SUMMARY OF THE INVENTION

Accordingly, a main object of the present invention is to provide a highly absorbent polymer which exhibits a high initial absorption rate upon contact with a large amount of an aqueous liquid, such as a body fluid (mainly urine) excreted from the human body, does not bring about an absorbing capacity blocking phenomenon, such as gel blocking, after the initial absorption, is free from a lowering in the absorbing capacity after swelling, and can satisfactorily exhibit the absorbing capacity thereof.

The present inventors have made various studies and, as a result, have found that when the crosslinking

degree of the surface of the conventional absorbent polymer comprising water-insoluble, hydrophilic, cross-linked polymer particles of an alkali metal salt of acrylic acid is enhanced, the resultant polymer exhibits an absorbing capacity much superior to the conventional absorbent polymers and can attain the above-described object of the present invention (first finding).

The present inventors have made additional various studies and, as a result, have found that a polymer having a particular structure exhibits an absorbing capacity much superior to that of the conventional absorbent polymers and can attain the above-described object of the present invention (second finding).

That is, the present inventors have found that a polymer comprising an absorbent polymer having an enhanced crosslinking density on the surface thereof can attain the above-described object and that a polymer having a particular structure can attain the above-described object.

The present invention (first invention) has been made based on the above-described first finding, and the above-described object has been attained by providing the following highly absorbent polymer. In the following description, the first invention refers to

the following invention.

An absorbent polymer comprising water-insoluble, hydrophilic, crosslinked polymer particles having carboxyl or carboxylate groups,

characterized in that said water-insoluble, hydrophilic, crosslinked polymer particles have an absorbing capacity satisfying the following requirements (i) to (iii), said absorbing capacity being imparted by enhancing the crosslinking density of the surfaces of said water-insoluble, hydrophilic, crosslinked polymer particles:

(i) the equilibrium swelling physiological saline absorption is 40 g/g (polymer) or more;

(ii) the physiological saline absorption is 3 ml or more as determined by swelling 0.3 g of the polymer with physiological saline for 10 sec; and

(iii) the time taken for 5 ml of physiological saline to pass through a cylinder (internal diameter: 10 mm) having a cross-sectional area of  $0.785 \text{ cm}^2$  is 40 sec or less after 0.05 g of the polymer is packed together with physiological saline into the cylinder and swollen with the physiological saline, reaches an equilibrium swelling physiological saline absorption and settles in a swollen state.

Further, the present invention (second invention)

has been based on the above-described first finding, and the above-described object has been attained by providing the following highly absorbent polymer. In the following description, the second invention refers to the following invention.

An absorbent polymer comprising water-insoluble, hydrophilic, crosslinked polymer particles having carboxyl or carboxylate groups,

characterized in that said water-insoluble, hydrophilic, crosslinked polymer particles have an absorbing capacity satisfying the following requirements (i) to (iii), said absorbing capacity being imparted by enhancing the crosslinking density of the surfaces of said water-insoluble, hydrophilic, crosslinked polymer particles:

(i) the equilibrium swelling physiological saline absorption is 40 g/g (polymer) or more;

(ii) the physiological saline absorption is 6 ml or more as determined by swelling 0.3 g of the polymer with physiological saline for 30 sec; and

(iii) the time taken for 50 ml of physiological saline to pass through a cylinder (internal diameter: 25.6 mm) having a cross-sectional area of 5.15 cm<sup>2</sup> is 150 sec or less after 0.5 g of the polymer is packed together with physiological saline into the cylinder and

swollen with the physiological saline, reaches an equilibrium swelling physiological saline absorption and settles in a swollen state.

Furthermore, the present invention (third invention) has been made based on the above-described second finding, and the following highly absorbent polymer is provided as an invention capable of attaining the above-described object. In the following description, the third invention refers to the following invention.

A highly absorbent polymer comprising an agglomerate comprised of water-insoluble, hydrophilic, cross-linked polymer particles having carboxyl or carboxylate groups, characterized by having a structure satisfying the following requirements (a) to (d):

(a) said particles constituting the agglomerate in such a manner that they have voids between themselves substantially communicating with the exterior of said agglomerate;

(b) the total volume of said voids is 0.2 cc/g (polymer) or more;

(c) said agglomerate is nonspherical and has a degree of irregular shape,  $P$ , of 1.2 or more; and

(d) the average particle diameter  $d_{50}$  (particle diameter corresponding to a cumulative particle diameter of 50%) of said agglomerate is in the range of from

100 to 500  $\mu\text{m}$ .

The highly absorbent polymer of the present invention exhibits a high initial rate of absorption of a large amount of an aqueous liquid, such as a body fluid (mainly urine), is free from the lowering in the absorbing capacity after the initial absorption, and can sufficiently exhibit the absorbing capacity of the absorbent polymer when used as an absorbent material such as a disposable diaper.

The "agglomerate" is a nodule made of the collecting the above-mentioned crosslinked polymer particles.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram showing a method for measuring the absorption as a measure of the absorption rate of the highly absorbent polymer together with an apparatus for the measurement.

Fig. 2 is a diagram showing a method for measuring the passing time for physiological saline (a factor for evaluating gel blocking tendency) together with an apparatus for the measurement.

#### DETAILED DESCRIPTION OF THE INVENTION

The highly absorbent polymer of the first and second inventions will now be described together with the method for producing the same. The term "highly absorbent polymer" is intended to mean only the highly

absorbent polymers of the first, second and third inventions for the purpose of distinguishing the highly absorbent polymer from the conventional "absorbent polymers". The term "absorption" is synonymous with "water absorption" and the term "absorption rate" is synonymous with "water absorption rate" in the present invention.

The expression "absorbent polymer comprising water-insoluble, hydrophilic, crosslinked polymer particles having carboxyl or carboxylate groups" used in the present invention is intended to mean conventional absorbent polymers produced by the method described in Japanese Patent Publication Nos. 74241/1991 and 30710/1979, etc., and there is no particular limitation on the method for producing such an absorbent polymer so far as the resultant polymer comprises water-insoluble, hydrophilic, crosslinked polymer particles. Preferred examples of the water-insoluble, hydrophilic, crosslinked polymer having carboxyl groups (or carboxylate groups) include a polymer produced by polymerizing a water-soluble, ethylenically unsaturated monomer having a carboxyl group.

Preferred examples of the water-soluble, ethylenically unsaturated monomer having a carboxyl group include polyacrylic acid (and its salts) and polymetha-

acrylic acid (and its salts). Further, it is possible to use polymers produced by copolymerizing acrylic or methacrylic acid with proper monomers such as maleic acid, itaconic acid, acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, 2-(meth)-acryloylethanesulfonic acid and 2-hydroxyethyl (meth)-acrylate.

The highly absorbent polymer of the first and second inventions is a polymer produced by enhancing the crosslinking density of the surface of the above-described absorbent polymer comprising water-insoluble, hydrophilic, crosslinked polymer particles (in the following description, when reference is made to "crosslinked polymer particles", the term "crosslinked polymer particles" are intended to mean the water-insoluble, hydrophilic, crosslinked polymer particles) to such an extent that the highly absorbent polymer exhibits an absorbing capacity capable of satisfying the above-described requirements (i) to (iii). Further, in the following description, when reference is made simply to "absorbent polymer," the term "absorbent polymer" is intended to mean mainly the absorbent polymer comprising crosslinked polymer particles.

The highly absorbent polymer of the first and second inventions can absorb and hold a large amount of an aqueous liquid by virtue of the above-described



absorbing capacity specified in the above item (i), can rapidly absorb the aqueous liquid during initial absorption by virtue of the absorbing capacity specified in the above item (ii) and can again absorb and hold the aqueous liquid until the absorption reaches the equilibrium swelling absorption of the polymer even after it has once absorbed the aqueous liquid by virtue of the absorbing capacity specified in the above item (iii) (by virtue of the freeness from gel blocking).

Further, in the highly absorbent polymer of the first and second inventions, the amount of the dissolution of the polymer in physiological saline is preferably 5% by weight or less (based on the polymer) from the viewpoint of the expected object.

The measurement of the absorbing capacities specified in the above items (i) to (iii) in the first and second inventions was conducted by the following methods (1) to (3). Further, the amount of dissolution of the polymer was determined by the following measuring methods (4).

(1) [Method for measuring equilibrium swelling  
absorption of highly absorbent polymer]

About 1 g of the polymer was dispersed in a large excess of physiological saline (0.9% saline) to swell the polymer until the absorption reaches the equilibri-

um swelling state. Then, the physiological saline was filtered through an 80-mesh gauze, the weight ( $W$ ) of the resultant swollen polymer was measured, and this value was divided by the weight ( $W_0$ ) of the polymer before the water absorption to provide a  $W/W_0$  value as the absorption (g/g) specified in the above item (i).

(2)[Method for measuring absorption as measure of absorption rate of highly absorbent polymer]

Use was made of an apparatus 1 (a Demand Wettability Tester) generally known as a device for practicing DW method and shown in Fig. 1. As shown in Fig. 1, 0.3 g of polymer P was spread on a polymer spreading stand 2 (a stand wherein No. 2 filter paper having a diameter of 70 mm was put on a glass filter No. 1) set in such a manner that the levels of the physiological saline W are equal to each other. The absorption at the time when the polymer was spread was taken as 0 (zero), and the adsorptions 10 sec and 30 sec after the spreading of the polymer were measured by reading the graduation of the buret indicating the degree of the lowering in the level of the physiological saline W. The measured value was taken as the absorption (ml) specified in the above item (ii).

(3)-(1) [Method for measuring passing time of physiological saline (factor showing evalua-

tion of gel blocking tendency))

The measurement of the absorbing capacities specified in the above item (iii) in the first invention was conducted by this method. This method is suitable for a polymer exhibiting a remarkably high rate of the solution passing time.

0.05 g of the polymer was packed into an apparatus 10 [a buret comprising a glass cylindrical tube having an inner diameter of 10.0 mm and a length of about 300 mm (a cylindrical portion)] shown in Fig. 2, and swollen with an excess of physiological saline until the swelling reached equilibrium. The level of the physiological saline was adjusted to a position corresponding to the liquid amount of 20 ml, and the cock was closed. After the polymer P was sufficiently settled as shown in Fig. 2, the cock was opened to measure the time taken for the physiological saline W (liquid amount : 5 ml) to pass through between two marked lines L (level of the liquid amount of 15 ml of the physiological saline) and M (level of the liquid amount of 10 ml of the physiological saline) shown in the figure, and this measured value was taken as the solution passing time (sec) specified in the above item (iii).

(3)-(2) [Method for measuring passing rate of physiological saline (factor showing evalua-

tion of gel blocking tendency)]

The measurement of the absorbing capacities specified in the above item (iii) in the second invention was conducted by this method. This method is suitable for a polymer exhibiting a high rate of the solution passing time.

0.5 g of the polymer was packed in an apparatus (a buret comprising a glass cylindrical tube equipped with a cock and having an inner diameter of 25.6 mm and a length of about 500 mm (a cylindrical portion)) which is similar to an apparatus 10 shown in Fig. 2 but having a larger scale than the apparatus 10 shown in Fig. 2, and swollen with an excess of physiological saline until the swelling reached equilibrium. The level of the physiological saline was adjusted to a position corresponding to the liquid amount of 200 ml, and the cock was closed. After the polymer P was sufficiently settled as shown in the figure, the cock was opened to measure the time taken for the physiological saline W (liquid amount: 50 ml) to pass through between two marked lines L (level of the liquid amount of 150 ml of the physiological saline) and M (level of the liquid amount of 100 ml of the physiological saline) shown in the figure, and this measured value was taken as the solution passing time (sec) specified in

the above item (iii).

(4) [Method for measuring amount of dissolution of highly absorbent polymer]

1 g of a highly absorbent polymer was accurately weighed into a beaker having a capacity of 300 ml, 150 ml of physiological saline was added thereto, and the mixture was allowed to stand at room temperature for about 15 h with occasional stirring to swell the polymer. Thereafter, about 30 ml (A ml) of the swollen polymer was weighed out, and treated on a Marusan Ultracentrifuge (available from Sakuma Seisakusho; Model 50s-2, angle rotor 1s) at 40,000 rpm (105,400G) and 25°C for 2 h. The supernatant was filtered, and the filtrate was diluted to 100 ml. 50 ml of the dilute solution was placed in a conical flask having a capacity of 100 ml, 10 ml of a 0.005 N methyl glycol chitosan solution was added thereto, the pH value was adjusted to about 11 with aqueous ammonia, and 2 to 3 drops of a Toluidine Blue solution were added thereto. Excess methyl glycol chitosan was titrated until the color of a 0.0025 N potassium polyvinylsulfate solution changes from blue to purplish red. Separately, a blank test was conducted in the same manner as that described above, and a calculation was conducted according to the following equation [Numerical formula 1] to determine

the amount (%) of dissolution of polymer.

[Numerical formula 1]

$$\begin{aligned} & \text{Amt. (\%)} \text{ of dissolution of polymer} \\ &= \frac{*94 \times 0.0025 (b - a)}{\text{Amt. (g) of sample} \times \frac{A}{150} \times \frac{50}{100} \times 1000} \times 100 \\ &= \frac{*94 \times 3 \times 0.0025 (b - a)}{\text{Amt. (g) of sample} \times A} \times 100 \end{aligned}$$

wherein a: represents the consumption (ml) of the  
0.0025 N potassium polyvinylsulfate solution  
in the main test, and

b: represents the consumption (ml) of the  
0.0025 N potassium polyvinylsulfate solution  
solution in the blank test.

The highly absorbent polymer of the first and second inventions is a polymer produced by enhancing the crosslinking degree of the surfaces of the above-described crosslinked polymer particles so as to impart the absorbing capacity specified in the above items (i) to (iii). There is no particular limitation on the method for producing the highly absorbent polymer. For example, the highly absorbent polymer can be produced by the following method.

Examples of the water-insoluble, hydrophilic, crosslinked polymer particle having carboxyl or carboxylate groups to be used in the production of the

highly absorbent polymer of the first and second inventions include absorbent polymers produced by the methods described in the above-described Japanese Patent Publication Nos. 74241/1991 and 30710/1979, etc., that is, absorbent polymer particles produced by polymerizing the conventional water absorbing polymer belonging to the category of the above-described crosslinked polymer particles, for example, a water-soluble, ethylenically unsaturated monomer containing a carboxyl group. It is also possible to use these polymers as produced without taking out them from the reaction system.

There is no particular limitation on the diameters of the crosslinked polymer particles, and the conventional absorbent polymer, as such, may be used. The particle diameter of the absorbent polymer is preferably 100 to 500  $\mu\text{m}$ .

Examples of dispersion media which may be used for dispersing the above-described crosslinked polymer particles in the production of the highly absorbent polymer of the first and second inventions include those used in the production of the above-described conventional absorbent polymers, that is, hydrocarbons and halogenated aromatic hydrocarbons, and specific examples thereof include aromatic hydrocarbons, such as

benzene, ethylbenzene, toluene and xylene, alicyclic hydrocarbons, such as cyclohexane, methylcyclohexane, cyclooctane and decalin, aliphatic hydrocarbons, such as hexane, pentane, heptane and octane, and halogenated hydrocarbons, such as chlorobenzene, bromobenzene and dichlorobenzene, among which toluene, xylene, cyclohexane, methylcyclohexane, hexane, heptane, chlorobenzene and chlorobenzene [sic] are preferred.

Examples of protective colloids which may be used in the production of the highly absorbent polymer of the first and second inventions through the utilization of reverse phase suspension polymerization include nonionic surfactants, such as sorbitan/fatty acid ester, polyglycerin/fatty acid ester, sucrose/fatty acid ester, sorbitol/fatty acid ester, polyoxyethylene alkyl ether, polyoxyethylene alkylphenyl ether, and polymeric protective colloids, such as cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate phthalate, ethylcellulose, benzylcellulose, ethylhydroxyethylcellulose, oxidized polyethylene, anhydrous maleinized polyethylene and anhydrous maleinized polybutadiene.

Examples of crosslinking agents which may be used in the production of the highly absorbent polymer of the first and second inventions include polyglycidyl



ethers, such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether and glycerin triglycidyl ether, haloepoxy compounds, such as epichlorohydrin and  $\alpha$ -methylchlorohydrin, polyaldehydes, such as glutaraldehyde and glyoxal, polyols, such as glycerin, pentaerythritol and ethylene glycol, and polyamines, such as ethylenediamine, among which those having a tri- or higher functional group are particularly preferred.

For example, specific embodiments of the method for producing the highly absorbent polymer of the first and second inventions are as follows.

1. A method which comprises dispersing and heating the above-described crosslinked polymer particles in a mixed solvent comprising the above-described dispersion medium and water (mixing rate: water/solvent of 50 to 5/50 to 95) and adding the above-described crosslinking agent to the heated dispersion to further catalytically react the crosslinking agent with the crosslinked polymer particles, thereby enhancing the crosslinking density of the surfaces of the crosslinked polymer particles.

2. A method which comprises dispersing and suspending an aqueous solution of a hydrophilic monomer having carboxyl groups (or carboxylate groups) and

containing an aqueous initiator in a nonaqueous solvent in the presence of a protective colloid, polymerizing the monomer to provide the above-described crosslinked polymer particles, regulating the water content of the crosslinked polymer particles in the solution to 10 to 40% by weight, and adding a crosslinking agent to further catalytically react the crosslinked polymer particles with the crosslinking agent to further crosslink the surfaces of the crosslinked polymer particles.

The amount of the crosslinking agent to be used in the method according to the present invention is preferably in the range of from 1,000 to 10,000 ppm based on the crosslinked polymer particle. The regulation of the amount of the crosslinking agent in the above-described range is suitable for producing a highly absorbent polymer comprising crosslinked polymer particles having an intended crosslinking density.

The highly absorbent polymer of the third invention will now be described.

The highly absorbent polymer of the third invention comprises an agglomerate comprised of the above-described crosslinked polymer particles having carboxyl or carboxylate groups and has a structure satisfying the above-described requirements (a) to (d).

Although the above-described particles constitut-

ing the highly absorbent polymer of the third invention may comprise substantially the same component as that of the crosslinked polymer particles constituting the above-described highly absorbent polymer of the first invention, the particles constituting the highly absorbent polymer of the second invention are different from the above-described crosslinked polymer in the structure (physical structure).

In the highly absorbent polymer of the third invention, as specified in the above item (a), the particles constituting the agglomerate in such a manner that they have voids between themselves substantially communicating with the exterior of the agglomerate, which enables an aqueous liquid to be easily absorbed into the highly absorbent polymer when the highly absorbent polymer comes into contact with the aqueous liquid.

In the highly absorbent polymer of the third invention, as specified in the above item (b), the total volume of the voids is 0.2 cc/g or more, preferably 0.3 cc/g or more. When the total volume of the voids is less than 0.2 cc/g, the function of temporarily stocking the liquid lowers, so that it becomes difficult to attain a satisfactory initial absorption rate. With consideration of the gel strength of poly-

mer particles after swelling, when the total volume of the voids is excessively large, the gel strength lowers, so that the swollen polymer is broken even by the application of a low pressure. For this reason, the total volume of the voids is preferably 1.0 cc/g or less. The above-described total volume of the voids was measured with a mercury porosimeter (Model 9220 Autopore manufactured by Shimadzu Corp.). This measuring method is based on such a principle that, since mercury can prevent the substance from leaking, the pressure is inversely proportional to the minimum void diameter which permits the mercury to intrude and the amount of intrusion of mercury is equal to the volume of the void.

As specified in the above item (c), the highly absorbent polymer of the third invention is nonspherical and has a degree of irregular shape,  $P$ , of 1.2 or more. This irregular shape can prevent the reduction of the voids due to rearrangement and adherence of particles after swelling. When the above-described degree of irregular shape is less than 1.2, the deformation value of an uneven portion of the surface of swollen particle becomes unsatisfactory, so that the voids defined by swollen particles cannot be maintained, which leads to the occurrence of gel blocking.

The above-described degree of irregular shape, P, represents the roughness of the highly absorbent polymer particles and can be defined by the following Numerical formula 2. Further, the actual area (S) and peripheral length (l) used in the calculation of the above-described degree of irregular shape, P, were measured by observing highly absorbent particles as projecting particles with an IV image processor EXCEL available from Nippon Avionics Co., Ltd.

[Numerical formula 2]

$$P = \frac{l}{L}$$

wherein P represents the degree of irregular shape, L represents the equivalent circumferential length of projection particle represented by the following Numerical formula 3, and l represents the peripheral length of the polymer particle,

[Numerical formula 3]

$$L = 2\pi r = 2\pi \sqrt{\frac{S}{\pi}} \dots\dots (1)$$

wherein s represents the actual area of projecting particle, and r represents the radius of equivalent circle.

Further, in the highly absorbent polymer of the third invention, as specified in the above item (d),

the average particle diameter (particle diameter corresponding to a cumulative particle diameter of 50%),  $d_{50}$ , is 100  $\mu\text{m}$  or more, preferably 150  $\mu\text{m}$  or more, and not more than 500  $\mu\text{m}$ . When the amount of fines becomes large, the proportion of the voids is reduced, so that gel blocking is liable to occur. On the other hand, when the particle diameter is excessively large, the application to an absorbent article brings about the feeling of physical disorder.

Although there is no particular limitation on the method for producing the highly absorbent polymer of the third invention, the highly absorbent polymer can be produced by the above-described method for producing the highly absorbent polymer of the first and second inventions.

The above-mentioned explanations referring to "the water-insoluble, hydrophilic, crosslinked polymer particles having carboxyl or carboxylate groups", "the water-soluble, ethylenically unsaturated monomer having a carboxyl group", etc. in the first and second inventions are applicable to the third invention.

When the highly absorbent polymer of the first and second inventions comes into contact with a large amount of an aqueous liquid, such as a body fluid (mainly urine), it absorbs and swells the aqueous

liquid as the conventional absorbent polymer does. Further, according to the highly absorbent polymer of the first invention, since the surface thereof has an enhanced crosslinking density, it is difficult for voids between polymers to be blocked. Further, after swelling, the tackiness of the surface of the swollen polymer is prevented, so that blocking among swollen polymers is less liable to occur. Further, it is considered that even when swollen polymers in contact with each other are partly adhered to each other, the adhesion occurs with the void being left among swollen polymers, so that the void portions serve as a passage of the aqueous liquid, whereby the diffusion of the aqueous liquid into the highly absorbent polymer as a whole is not inhibited by the swollen polymer. Moreover, it is considered that the absorption rate is high because the surface of the highly absorbent polymer has a crosslinking structure which accelerates the absorption of the aqueous liquid which has come into contact with the surface of the highly absorbent polymer into the highly absorbent polymer.

It is estimated that the highly absorbent polymer of the first and second inventions exhibits the absorbing capacity specified in the above items (i) to (iii) by virtue of the above-described functions.

Further, it is estimated that since the highly absorbent polymer of the third invention comprises an agglomerate having a structure satisfying the above-described requirements (a) to (d), it exhibits substantially the same function as that of the highly absorbent polymer of the first and second inventions, which enables the absorbing capacity specified in the above items (i) to (iii) to be exhibited.

#### Example 1

A 500-ml four-necked round-bottom flask equipped with a stirrer, a reflux condenser, a dropping funnel and a nitrogen gas feed pipe was charged with 230 ml of cyclohexane and 1.4 g of sorbitan monostearate (Span 60), and the mixture was stirred to provide a homogeneous solution. Separately, 30 g of an acrylic acid monomer was neutralized in a conical flask with 13.4 g of caustic soda dissolved in 39 g of water. The aqueous acrylic acid monomer had a monomer concentration of 45% (water content: 55%). Then, 0.1 g of potassium persulfate was dissolved in the aqueous monomer solution. This aqueous monomer solution was dropwise added to the above-described four-necked flask containing cyclohexane, etc., in a nitrogen atmosphere. The mixture was heated to 70 to 75°C to initiate polymerization.



The water content of the polymer suspended in cyclohexane was regulated to 35%, 27% and 20% by azeotropic dehydration (under reflux of cyclohexane). Thereafter, a solution of 0.03 g of ethylene glycol diglycidyl ether in 1 ml of water was added to each suspension at 73°C. The system was maintained at that temperature for 2 h, and cyclohexane was removed therefrom. The resultant polymers were dried in vacuo at 80 to 100°C to provide highly absorbent polymers A, B and C (products of the present invention) listed in the following Table 1.

#### Example 2

40 g of each of the highly absorbent polymers A, B and C produced in the Example 1 together with 230 ml of cyclohexane was placed again in the 500-ml four-necked round-bottom flask, water was added thereto, the water contents of the polymers were regulated respectively to 35%, 27% and 20%, and each system was heated to 75°C. After the temperature becomes constant, ethylene glycol diglycidyl ether (2500 ppm based on the polymer) was added to each system. After the mixture was maintained at 75°C for 3h, cyclohexane was removed therefrom and the resultant polymers were dried in vacuo at 80 to 100°C to provide highly absorbent polymers D, E and F (products of the present invention) listed in the

following Table 1.

#### Example 3

A highly absorbent polymer G (product of the present invention) listed in the following Table 1 was produced in the same manner as that used in the production of the highly absorbent polymer A in the Example 1, except that the crosslinking agent (ethylene glycol diglycidyl ether) was previously added to the aqueous monomer solution instead of the addition of the crosslinking agent after the completion of the regulation of the water content.

#### Example 4

72.1 g of acrylic acid was diluted with 18.0 g of water and neutralized with 98.9 g of a 30 wt.% aqueous sodium hydroxide solution under cooling, and 10.7 g of a 2.8 wt.% aqueous 2,2'-azobis(2-amidinopropane) dihydrochloride solution was added thereto to prepare a homogeneous solution as an aqueous monomer/initiator solution.

Separately, a 500-ml flask equipped with a reflux condenser, a dropping funnel, a stirring rod and a nitrogen gas feed pipe was charged with 283 ml of cyclohexane, and 2.2 g of a 25 wt.% aqueous solution of sodium salt of polyoxyethylene dodecyl ether sulfate [average number of moles of addition of ethylene oxide:

2] was added thereto. They were stirred (at 300 rpm) and dispersed in each other, and the flask was purged with nitrogen and heated to 75°C. The above-described aqueous monomer/initiator solution was dropwise added thereto over a period of 30 min. After the completion of the addition, the system was subjected to polymerization with stirring at 75°C for 1.5 h and at 80°C for 4 h.

After the completion of the polymerization, the product was fractionated and dried under reduced pressure to provide 88.4 g of a polymer of acrylic acid (sodium salt). The resultant polymer was a granular material having a distorted shape of 400  $\mu\text{m}$  in the average particle diameter as measured by sieving and a bulk density of 0.41 g/ml. The surface of the polymer particle had such a structure that particles having an irregular shape of several to 20  $\mu\text{m}$  in the size were fused to each other, and the unevenness of the surface was very significant.

The resultant polymer (product of the present invention Q) was subjected to measurement of the equilibrium swelling water absorption, water absorption as a measure of the water absorption rate, physiological saline passing time, etc. The results are given in Table 1.

#### Example 5

72.1 g of acrylic acid was diluted with 32.0 g of water and neutralized with 98.9 g of a 30 wt.% aqueous sodium hydroxide solution under cooling, and 10.7 g of a 2.8 wt.% aqueous potassium persulfate solution was added thereto to prepare a homogeneous solution as an aqueous monomer/initiator solution.

Separately, a 500-ml flask equipped with a reflux condenser, a dropping funnel, a stirring rod and a nitrogen gas feed pipe was charged with 283 ml of cyclohexane, and 1.5 g of a 25 wt.% aqueous solution of sodium salt of polyoxyethylene dodecyl ether sulfate [average number of moles of addition of ethylene oxide: 3] was added thereto. They were stirred (at 300 rpm) and dispersed in each other, and the flask was purged with nitrogen and heated to 75°C. The above-described aqueous monomer/initiator solution was dropwise added thereto over a period of 30 min. In this case, 0.058 g of ethylene glycol diglycidyl ether was simultaneously dropwise added as an epoxy bifunctional crosslinking agent in portions through a syringe. After the completion of the dropwise addition, the system was subjected to polymerization with stirring at 75°C for 1.5 h and at 80°C for 4 h.

After the completion of the polymerization, the

product was fractionated and dried under reduced pressure to provide 88.4 g of a polymer of acrylic acid (sodium salt). The resultant polymer was a granular material having a distorted shape of 400  $\mu\text{m}$  in the average particle diameter as measured by sieving and a bulk density of 0.41 g/ml. The surface of the polymer particle had such a structure that particles having an irregular shape of several to 20  $\mu\text{m}$  in the size were fused to each other, and the unevenness of the surface was very significant.

The resultant polymer (product of the present invention R) was subjected to measurement of the equilibrium swelling water absorption, water absorption as a measure of the water absorption rate, physiological saline passing time, etc. The results are given in Table 1.

#### Example 6

72.1 g of acrylic acid was diluted with 18.0 g of water and neutralized with 98.9 g of a 30 wt.% aqueous sodium hydroxide solution under cooling, and 5.6 g of a 5.2 wt.% aqueous potassium persulfate solution was added thereto to prepare a homogeneous solution as an aqueous monomer/initiator solution.

Separately, a 500-ml flask equipped with a reflux condenser, a dropping funnel, a stirring rod and a

nitrogen gas feed pipe was charged with 283 ml of cyclohexane, and 1.8 g of dodecylglucoside (rate of condensation : 1.25) was added thereto. They were stirred (at 300 rpm) and dispersed in each other, and the flask was purged with nitrogen and heated to 75°C. The above-described aqueous monomer/initiator solution was dropwise added thereto over a period of 30 min. After the completion of the dropwise addition, the system was subjected to polymerization with stirring at 75°C for 1.5 h and at 80°C for 4 h.

After the completion of the polymerization, the product was fractionated and dried under reduced pressure to provide 88.4 g of a polymer of acrylic acid (sodium salt). The resultant polymer was a granular material having a distorted shape of 650  $\mu\text{m}$  in the average particle diameter as measured by sieving and a bulk density of 0.30 g/ml. The surface of the polymer particle had such a structure that particles having an irregular shape of several to 20  $\mu\text{m}$  in the size were fused to each other, and the unevenness of the surface was very significant.

The resultant polymer (product of the present invention S) was subjected to measurement of the equilibrium swelling water absorption, water absorption as a measure of the water absorption rate, physiological

saline passing time, etc. The results are given in Table 1.

#### Example 7

72.1 g of acrylic acid was diluted with 18.0 g of water and neutralized with 98.9 g of a 30 wt.% aqueous sodium hydroxide solution under cooling, and 10.7 g of a 2.8 wt.% aqueous potassium persulfate solution was added thereto to prepare a homogeneous solution as an aqueous monomer/initiator solution.

Separately, a 500-ml flask equipped with a reflux condenser, a dropping funnel, a stirring rod and a nitrogen gas feed pipe was charged with 283 ml of cyclohexane, and 0.55 g of trimethylstearylammmonium chloride was added thereto. They were stirred (at 300 rpm) and dispersed in each other, and the flask was purged with nitrogen and heated to 75°C. The above-described aqueous monomer/initiator solution was dropwise added thereto over a period of 30 min. After the completion of the dropwise addition, the system was subjected to polymerization with stirring at 75°C for 1.5 h and at 80°C for 4 h.

After the completion of the polymerization, the product was fractionated and dried under reduced pressure to provide 88.4 g of a polymer of acrylic acid (sodium salt). The resultant polymer was a granular

material having a distorted shape of 800  $\mu\text{m}$  in the average particle diameter as measured by sieving and a bulk density of 0.54 g/ml. The surface of the polymer particle had such a structure that particles having an irregular shape of several to 20  $\mu\text{m}$  in the size were fused to each other, and the unevenness of the surface was very significant.

The resultant polymer (product of the present invention T) was subjected to measurement of the equilibrium swelling water absorption, water absorption as a measure of the water absorption rate, physiological saline passing time, etc. The results are given in Table 1.

#### Comparative Example 1

Highly absorbent polymers H, I and J (comparative products) listed in the following Table 2 were produced in the same manner as that used in the production of the highly absorbent polymers A to C in the Example 1, except that the solution contained in the above-described four-necked round-bottom flask charged with cyclohexane, etc., was heated to 70 to 75°C, the aqueous monomer solution was dropwise added thereto in a nitrogen atmosphere over a period of 1.5 h to conduct polymerization and the mixture was maintained at 70 to 75°C for 0.5 h to complete the polymerization.



#### Comparative Example 2

Absorbent polymers K, L and M (comparative products) listed in the following Table 2 were produced in the same manner as that used in the production of the absorbent polymers H to I in the Comparative Example 1, except that 1.94 g of ethylcellulose N-200 was used as the dispersion medium instead of Span 60.

#### Comparative Example 3

Three types of commercially available crosslinked polysodium acrylate (trade names: Alon ZAP RSII, Aqua Keep 10SH-P and Aqualic XAW-4) were used as highly absorbent polymers N, C and P (comparative products). See the following Table 2.

Table 1

	Total vol. of voids (cc/g)	Particle diam ( $\mu$ m)	Degree of irregular (P)	Absorp -tion (g/g)*1	Amount of dissoln. of polymer (%)	absorption		Passing time	
						(ml/10sec) * 2	(ml/30sec) * 3	(sec) * 4.0	(sec) * 5
A	0.32	235	1.32	76	7.0	6.5	12.1	18.0	40.0
B	0.28	235	1.36	78	6.5	6.0	12.4	24.0	58.0
C	0.26	235	1.28	70	7.0	5.4	12.0	30.0	77.0
D	0.32	220	1.33	52	0.2	6.0	11.8	12.0	32.0
E	0.31	220	1.32	53	0.1	6.0	11.7	14.0	34.0
F	0.32	220	1.29	65	0.1	6.2	12.0	12.0	30.0
G	0.28	240	1.28	48	3.8	4.5	10.2	35.0	82.0
Q	0.41	400	—	53.3	—	1.8	6.2	13.0	24.0
R	0.41	400	—	50.5	—	3.2	10.6	20.0	43.4
S	0.34	650	—	55.0	—	1.1	6.7	15.0	28.3
T	0.54	800	—	55.4	—	3.4	11.3	21.0	43.5

\*1 Equilibrium swelling absorption    \*2 Absorption after 10 sec    \*3 Absorption after 30 sec  
 \*4 Solution passing time of the liquid amount of 5 ml    \*5 Solution passing time of the liquid amount of 50 ml

Table 2

	Total vol. of voids (cc/g)	Particle diam. ( $\mu$ m)	Degree of irregular (P)	Absorp -tion (g/g)*1	Amount of dissoln. of polymer (%)	absorption		Passing time	
						(ml/10sec) *2	(ml/30sec) *3	(sec) *4	(sec) *5
H	0.01	205	1.11	65	0.2	1.0	4.0	176	670
I	0.04	205	1.05	70	0.1	1.2	4.3	136	435
J	0.04	205	1.18	69	0.1	1.1	4.2	134	433
K	0.00	140	1.01	68	0.1	1.2	3.9	198	638
L	0.00	140	1.02	72	0.2	1.5	4.0	164	577
M	0.00	140	1.01	63	0.3	1.1	3.8	166	582
N	0.09	360	1.30	60	3.9	1.0	3.4	17	33.0
O	0.18	240	1.29	64	6.8	4.5	12.1	105	259
P	0.05	480	1.26	54	5.2	1.3	4.5	13	47.0

\*1 Equilibrium swelling absorption \*2 Absorption after 10 sec \*3 Absorption after 30 sec

\*4 Solution passing time of the liquid amount of 5 ml \*5 Solution passing time of the liquid amount of 50 ml

## CLAIMS

1. A highly absorbent polymer comprising water-insoluble, hydrophilic, crosslinked polymer particles having carboxyl or carboxylate groups,

characterized in that said water-insoluble, hydrophilic, crosslinked polymer particles have an absorbing capacity satisfying the following requirements (i) to (iii), said absorbing capacity being imparted by enhancing the crosslinking density of the surfaces of said water-insoluble, hydrophilic, crosslinked polymer particles:

(i) the equilibrium swelling physiological saline absorption is 40 g/g (polymer) or more;

(ii) the physiological saline absorption is 3 ml or more as determined by swelling 0.3 g of the polymer with physiological saline for 10 sec; and

(iii) the time taken for 5 ml of physiological saline to pass through a cylinder (internal diameter: 10 mm) having a cross-sectional area of  $0.785 \text{ cm}^2$  is 40 sec or less with 0.05 g of the polymer, which has absorbed an equilibrium amount of physiological saline, being retained in a settled state within the cylinder.

2. A highly absorbent polymer according to claim 1, characterized in that said time in the above item (iii) of claim 1 is 20 sec or less.

3. A highly absorbent polymer comprising water-insoluble, hydrophilic, crosslinked polymer particles having carboxyl or carboxylate groups,

characterized in that said water-insoluble, hydrophilic, crosslinked polymer particles have an absorbing capacity satisfying the following requirements (i) to (iii), said absorbing capacity being imparted by enhancing the crosslinking density of the surfaces of said water-insoluble, hydrophilic, crosslinked polymer particles:

(i) the equilibrium swelling physiological saline absorption is 40 g/g (polymer) or more;

(ii) the physiological saline absorption is 6 ml or more as determined by swelling 0.3 g of the polymer with physiological saline for 30 sec; and

(iii) the time taken for 50 ml of physiological saline to pass through a cylinder (internal diameter: 25.6 mm) having a cross-sectional area of  $5.15 \text{ cm}^2$  is 150 sec or less after 0.5 g of the polymer is packed to-

gether with physiological saline into the cylinder and swollen with the physiological saline, reaches an equilibrium swelling physiological saline absorption and settles in a swollen state.

4. A highly absorbent polymer according to claim 3, characterized in that said physiological saline absorption in the above item (ii) of claim 3 is 9 ml or more.

5. A highly absorbent polymer according to claim 3 or 4, characterized in that said time in the above item (iii) of claim 3 is 75 sec or less.

6. A highly absorbent polymer according to any of claim 1 to 5, characterized in that the amount of dissolution of the polymer in the physiological saline is 5% by weight or less (based on the polymer).

7. A highly absorbent polymer comprising an agglomerate comprised of water-insoluble, hydrophilic, cross-linked polymer particles having carboxyl or carboxylate

groups, characterized by having a structure satisfying the following requirements (a) to (d):

(a) said particles constituting the agglomerate in such a manner that they have voids between themselves substantially communicating with the exterior of said agglomerate;

(b) the total volume of said voids is 0.2 cc/g (polymer) or more;

(c) said agglomerate is nonspherical and has a degree of irregular shape,  $P$ , of 1.2 or more; and

(d) the average particle diameter  $d_{50}$  (particle diameter corresponding to a cumulative particle diameter of 50%) of said agglomerate is in the range of from 100 to 500  $\mu\text{m}$ .

8. A highly absorbent polymer according to claim 7, characterized in that the amount of dissolution of the polymer in physiological saline is 5% by weight or less (based on the polymer).

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**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**Section 17 (The Search Report)**

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**Relevant Technical fields**

(i) UK CI (Edition L ) C3P - PFE, PFF  
 C3J - JAB, JCK

(ii) Int CI (Edition 5 ) C08F, C08L

**Search Examiner**

M J PRICE

**Databases (see over)**

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

**Date of Search**

16 AUGUST 1993

Documents considered relevant following a search in respect of claims

1-6

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X	GB A 2179663	(KAO)	1-6
X	GB A 2155020	(KAO)	1-6
X	GB A 2126591	(KAO)	1-6
X	GB A 2119384	(NIPPON)	1-6
X	EP 0317106	(NIPPON)	1-6
X	US 5055501	(NIPPON)	1-6
X	US 5053460	(HOECHST)	1-6
X	US 4507438	(SEITETSU)	1-6
X	US 4340706	(SEITETSU)	1-6



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